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Combining Ion-Exchange (IX) Technology and Biological Reduction for Perchlorate Removal

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Ion-exchange (IX) resin is perhaps the most promising technology to remove the contaminant perchlorate (ClO_4^-) from waters. However, ion exchange is only a separation technology that transfers the perchlorate from waters to the waste solutions used to regenerate the resins. The waste solutions contain high perchlorate concentrations, and treatment technologies for these regenerant solutions are needed. In this article, we review the latest knowledge on perchlorate removal by ion-exchange resins, propose three systems that combine ion-exchange resins (for perchlorate removal) and biological reduction for treating the waste solutions resulting from resin regeneration, and discuss the challenges and research needed to fully develop the proposed technology. © 2002 Wiley Periodicals, Inc.

INTRODUCTION

In the southwestern United States, perchlorate (ClO_4^-) contamination has been detected in waters and soils near facilities that manufactured or utilized sodium, potassium, and ammonium perchlorate salts. The concentration of this contaminant varies depending on the site; with many measurements in the parts per million (ppm) range in locations where perchlorate was manufactured (Boralessa, 2001). In other sites, where perchlorate contamination is associated with the migratory plumes resulting from the use of perchlorate in rocket and explosive manufacturing, perchlorate levels in the parts per billion (ppb) range are found (Gingras & Batista, 2002). The presence of perchlorate in waters has become a concern because of its interference with the normal functioning of the human thyroid gland. In March 2002, the USEPA National Center for Environmental Assessment issued a report recommending a standard of 1 part per million (ppm) for perchlorate in drinking waters (EPA, 2002), making remediation of perchlorate contaminated waters necessary.

With regulatory standards looming in the future, the search for effective means to remove perchlorate from waters is intensifying. Several technologies, including chemical reduction, carbon adsorption, membrane filtration (Yoon et al., 2000), biological reduction (Miller & Logan, 2000; Herman & Frankenberger, 1999; Rittmann & Nerenberg, 2000; Liu & Batista, 2000), and ion exchange (Tripp & Clifford, 2000a; Batista et al., 2000; Gu et al., 2000a) have been investigated. Thus far, biological reduction and ion exchange seem to be the most promising. While the water industry is familiar with the use of ion exchange because of its historic use for hardness and nitrate removal, the industry is not very comfortable with the intentional introduction of microorganisms to the water treatment train. Thus it is likely that biological reduction of perchlorate will not be used for perchlorate removal from drinking waters. Ion

exchange will be probably the technology of choice to remove perchlorate from several contaminated drinking waters. Ion-exchange, however, does not eliminate perchlorate from the environment; it transfers perchlorate from waters to the brine solutions used to regenerate the resins. The concentrated waste regenerant solutions contain high levels of perchlorate, and treatment technologies for these solutions are needed.

This article reviews the latest knowledge on perchlorate removal and anion competition by ion-exchange resins; introduces the potential treatment of ion-exchange waste regenerant solutions by biological reduction; discusses the effects of brine composition on perchlorate biodegradation; and assess additional work that needs to be accomplished to fully develop this technology.

PERCHLORATE REMOVAL BY ION-EXCHANGE RESINS

Resin Characteristics Affecting Perchlorate Removal

Strong-base anionic resins (SBAX) and weak-base anionic resins (WBAX) with both styrenic and acrylic matrices have been evaluated for their potential to remove perchlorate from waters. The affinity between the perchlorate ion and IX resins is high and the intensity of this affinity depends upon the interactions between perchlorate, the resin matrix, and the functional groups attached to the resin. Perchlorate is a large ($58.8 \text{ cm}^3/\text{g-mole}$) single-charged anion with a hydration number of four (Schilt, 1979). These physical characteristics have led to the classification of perchlorate as a poorly hydrated, hydrophobic anion (Guter, 2000; Gu et al., 2000b). Thus higher affinity should exist between IX resins with hydrophobic matrices (e.g., styrenic type resin) and perchlorate.

The work of Tripp and Clifford (2000b and 2002) demonstrates that the two most significant factors controlling the affinity between perchlorate and IX resins are the type of *resin matrix* and the type of *functional group* attached to the resin. Higher separation factors were found for polystyrenic (more hydrophobic) as compared to polyvinylpyridine and polyacrylic type resins, respectively. The results of fixed-bed column testing by Batista et al. (2000) agree with the observations of Tripp and Clifford.

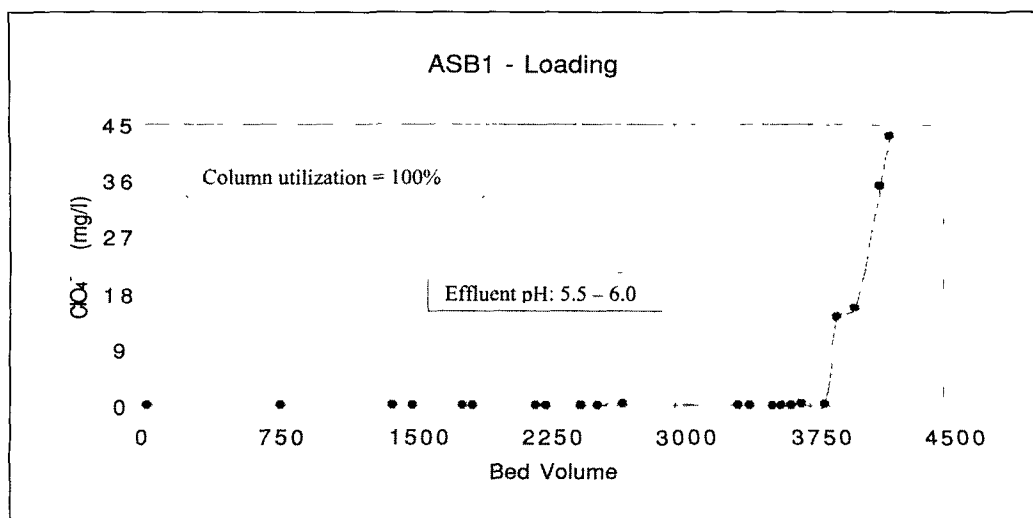


Exhibit 1a. Exhaustion of ASB1 resin (styrenic DVB-quaternary amine); fed with 40 mg/l synthetic perchlorate solution, EBCT = 4.9 minutes and BV = 117.84.

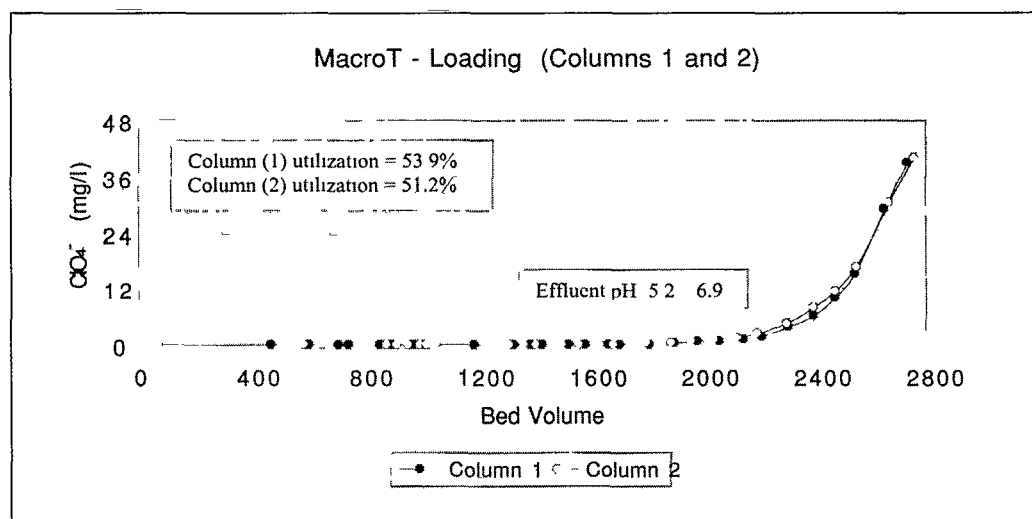


Exhibit 2a. Exhaustion of Macro-T resin (polyacrylic-quaternary amine); fed with 40 mg/l synthetic perchlorate solution, EBCT = 4.2 minutes, BV = 54.78 cm³ (column 1), EBCT = 4.4 minutes, and BV = 53.01 cm³ (column 2).

Exhibits 1a and 2a (Vieira, 2000) show breakthrough curves for perchlorate using styrenic and acrylic type resins, both with a quaternary trimethyl amine functional group. Both resins were able to remove perchlorate to very low levels, but the acrylic resin showed a smaller column utilization rate and less bed volumes treated.

The degree of cross-linking and resin porosity was found to be of minor significance in determining the affinity between perchlorate and IX resins (Tripp & Clifford, 2000a). Gregor et al. (1954) also demonstrated that changing the percent cross-linking from 3 percent to 16 percent has only a minor effect on the separation factors of quaternary ammonium anion-exchange resins toward perchlorate. In addition, Gregor et al. (1954) reported that the affinity of perchlorate toward resins varies with the resin loading. Selectivity coefficients approximately tripled as the amount of perchlorate in the resin increased. Gregor et al. (1954) attributed this anomaly to the formation of perchlorate ion-pairs bounded to functional sites within the resin (Guter, 2000). Gu et al. (2002) also found experimentally that perchlorate exchange into ion-exchange resins was concentration dependent, with non-linear isotherms observed at very high perchlorate loading. However, they did not suggest this observation was due to the formation of ion-pairs within the resin functional groups.

Regeneration of Perchlorate-Laden Resins

The high affinity of perchlorate for IX resins makes regeneration of spent resins very difficult. The more affinity the resin has for perchlorate the harder it is to be regenerated. As expected, styrenic SBAX resins regenerate poorly while acrylic ones generate very well. Exhibits 1b and 2b depict the regeneration curves for a spent column of styrenic and acrylic matrix resin, respectively. For the same concentration of regenerant (12 percent NaCl) and the same bed volumes (BV) of regenerant applied, 100 percent of perchlorate was removed from the acrylic resin, while only about 38 percent was removed from the styrenic resin. Separation coefficients are indicative of the relative affinity between the resin and the anion of concern. The higher the

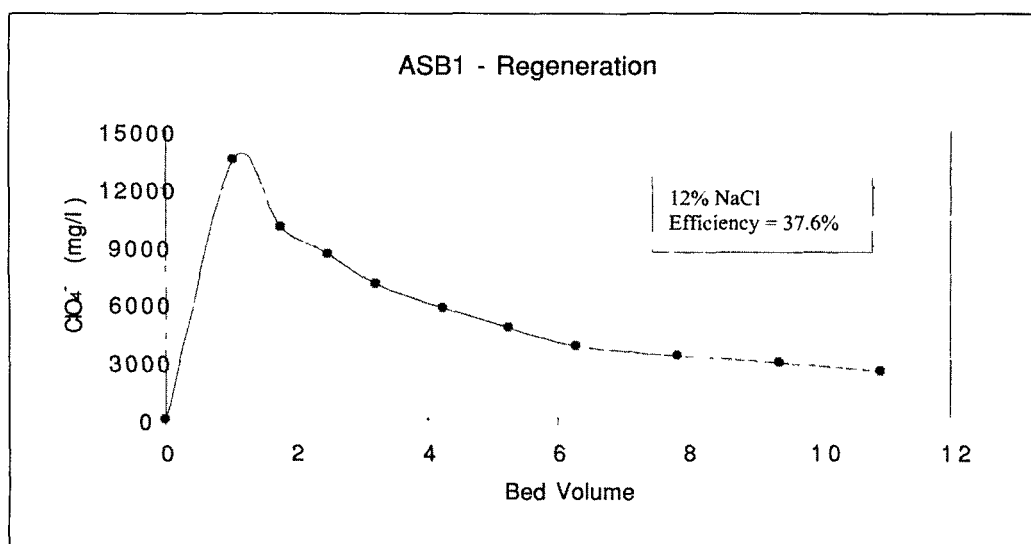


Exhibit 1b. Regeneration of ASB1 resin (styrenic DVB-quaternary amine) with 12 percent NaCl, EBCT = 7.8 minutes, and BV = 96.94 cm³.

separation coefficient, the greater the affinity of the resin for the ion. The separation coefficients for perchlorate were determined for acrylic resins as ($\alpha = 6$) and for styrenic as ($\alpha = 125$) (Tripp & Clifford, 2002). These coefficients also indicate a higher affinity of perchlorate for styrenic than for acrylic resins.

In addition to strong base anionic resins, weak base resins have also been investigated for perchlorate removal. Batista et al. (2000) reports that weak-base anionic resins are also capable of removing perchlorate from waters to very low levels. The acrylic-type WBAX can be completely regenerated with either NaCl or caustic solutions. The styrenic-type WBAX cannot be economically regenerated. Exhibits 3a and 3b (Vieira, 2000) show the loading and regeneration of a WBAX loaded with perchlorate. In the absence of other anions, more than 2800 BV (data not shown) could be processed before breakthrough (Vieira, 2000). In the presence of other anions (Exhibit 3a) the BV processed reduced to 900. However, the resin was 100 percent regenerated using 1 percent NaOH (Exhibit 3b).

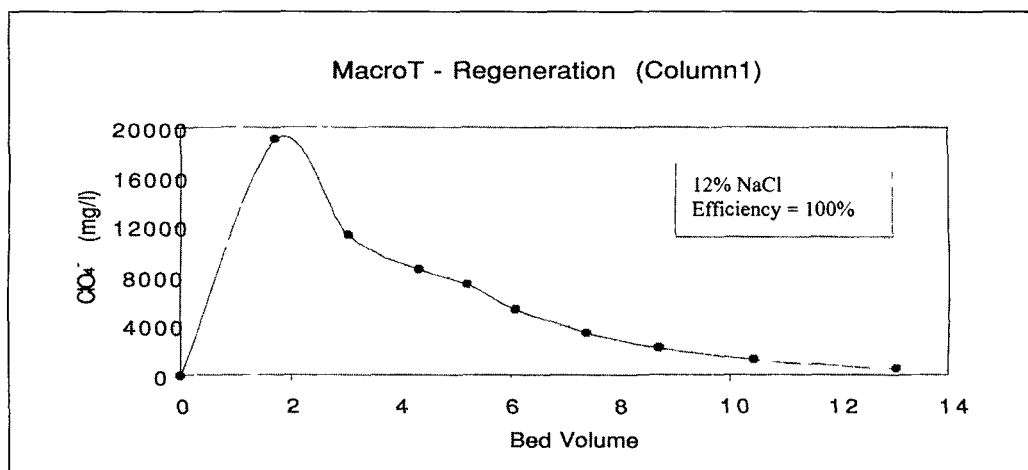


Exhibit 2b. Regeneration of Macro-T resin (polyacrylic-quaternary amine) with 12 percent NaCl, EBCT = 4.4 minutes, and BV = 54.78 cm³.

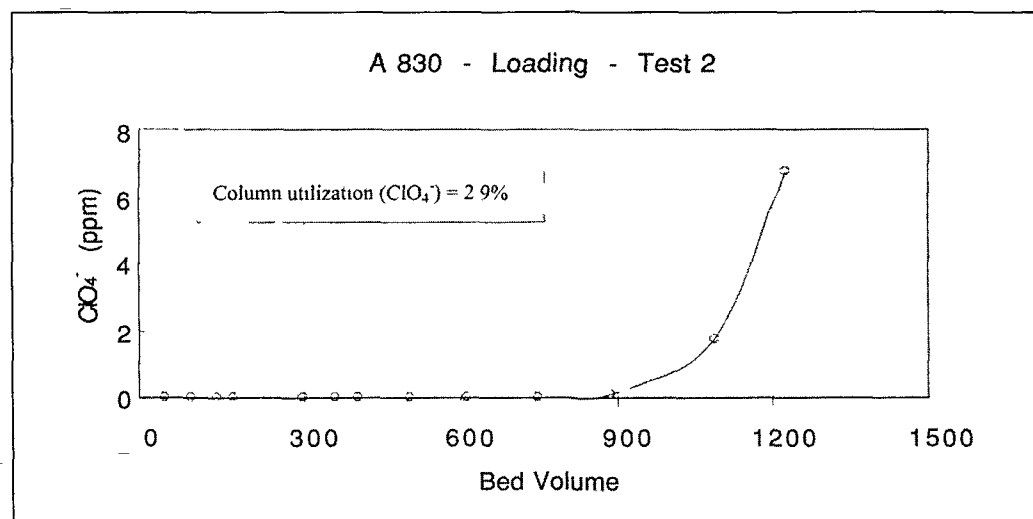


Exhibit 3a. Exhaustion of A 830 resin (acrylic-tertiary amine), Test 2, fed with synthetic solution containing 10 mg/l perchlorate, 100 mg/l sulfate, 100 mg/l nitrate, and 100 mg/l chloride EBCT = 4.5 minutes, BV = 55 67 cm³

The type of functional group attached to the resin also affects perchlorate removal. Tripp and Clifford (2000a) found that as the length of the alkyl group on the quaternary amine increases from methyl to ethyl and then to propyl, the separation factor increased from 125 to 1,100 and then 1,500, respectively. Unfortunately, the functional groups that provided higher affinity were found to have very slow kinetics.

In an effort to enhance the kinetics of perchlorate exchange, a perchlorate selective biofunctional resin, which had been used previously to remove pertechnetate from waters, has been evaluated for perchlorate removal (Brown et al., 2000). The resin contains two functional groups: a long chain quaternary ammonium group to improve selectivity and a short chain quaternary group to aid kinetics. Gu et al. (2002) reports that the bifunctional resin is capable of removing perchlorate from waters to undetectable levels and has separation factors three to ten times greater than those of monofunctional resins.

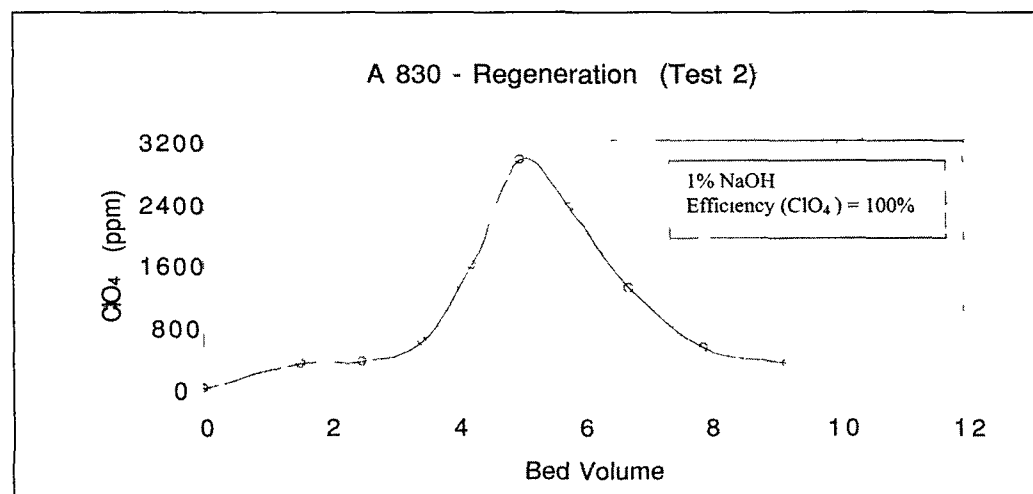


Exhibit 3b. Regeneration of A 830 resin, Test 2 (acrylic-tertiary amine) with 1 percent NaOH

Regeneration of Perchlorate-Laden Resins

Despite the effectiveness of ion exchange in removing perchlorate from waters, several issues deserve further consideration before this technology is implemented in full-scale water treatment plants. These issues include resin regeneration, competition of other anions, and treatment of regenerant solutions. Some progress has been made in the regeneration of perchlorate laden resins. Heating resins to 60 °C has proven to considerably increase the potential for perchlorate release from the resins (Tripp & Clifford, 2000a). Acrylic-type resins have been shown to regenerate much easier than their styrenic counterparts. Tetrachloroferrate (FeCl_4^-) has been shown to provide 100 percent regeneration of selective bifunctional resins after repeated loading and regeneration cycles (Gu et al., 2000, 2002). However, in a field trial significant fouling of the bifunctional resin was observed as the result of the precipitation of iron oxyhydroxides. About 30 to 40 percent of the resin capacity was lost after regeneration. The introduction of a 0.5 micron filter, before the resin bed, significantly decreases the fouling problem (Gu et al., 2002). Calgon Corporation developed a proprietary catalytic regeneration system (PNDM), using ammonium chloride, to reduce nitrate and perchlorate in ion exchange brines (Gingras & Batista, 2002). Calgon claims the system reduces nitrate and perchlorate to undetectable levels.

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Competition of Other Anions with Perchlorate

All waters contaminated with perchlorate will contain other anions such as nitrate, sulfate, chlorate, and bicarbonate. These anions compete for exchange sites in the resin and may decrease the resin's capacity for perchlorate. Selectivity coefficient determinations and computer modeling (Tripp & Clifford, 2002) have demonstrated that acrylic resins are more suitable for perchlorate contaminated waters with low sulfate concentration. Styrenic and selective resins work best for waters containing high sulfate concentrations. Resins traditionally used for nitrate removal are more suitable to treat perchlorate contaminated waters with high nitrate concentrations.

Exhibit 4 shows the loading of an acrylic-type resin with synthetic water containing sulfate, nitrate, chloride, and perchlorate. When perchlorate alone was loaded, more than 2,800 BV were processed before breakthrough (Vieira, 2000). That number was reduced to less than 1,000 BV in the presence of other anions. Notice that sulfate breakthrough occurred after 450 BV followed by nitrate at 760 BV.

The effects of several anions and humic substances (measured as TOC) on the removal of perchlorate by IX resins are depicted in Exhibits 5 and 6. The water used in this experiment is the highly perchlorate contaminated groundwater from the Muddy Creek aquifer in Henderson, Nevada (Exhibit 5). For the styrenic resin (Exhibit 5) the BV processed before perchlorate breakthrough was reduced from 3,750 to about 600 BV. Sulfate and nitrate breakthrough occurred almost immediately. For the acrylic resin, the capacity was reduced from 2,100 BV to zero. The resin could remove no anions from this water. The reason for that is the high amount of humic substances (measured as TOC) in the water. It was observed that after a few BV run, both the styrenic and the acrylic resins turned black, indicating fouling of the resin by humic substances. Thus the presence of humic acids interferes with perchlorate removal by ion-exchange resins. This effect is more pronounced in acrylic resins, where perchlorate exchange is completely hindered.

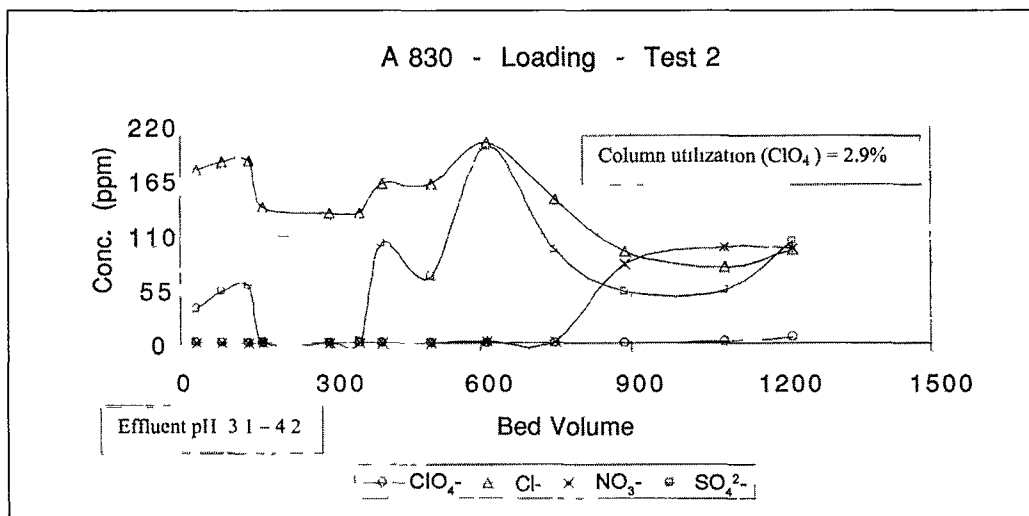


Exhibit 4. Exhaustion of A 830 resin (acrylic-tertiary amine), Test 2, fed with synthetic solution containing 10 mg/l perchlorate, 100 mg/l sulfate, 100 mg/l nitrate, and 100 mg/l chloride. EBCT = 4.5 minutes, BV = 55.67 cm³

BIOLOGICAL REDUCTION OF PERCHLORATE IN WASTE BRINES FROM IX

Types of Solutions Used to Regenerate Spent Resins and Potential for Biodegradation

Regeneration of spent resin requires the application of a regenerant solution to remove perchlorate and other anions from the ion-exchange bed. The regenerated resin can then be reused, making the process economically viable. The type of regenerant used depends

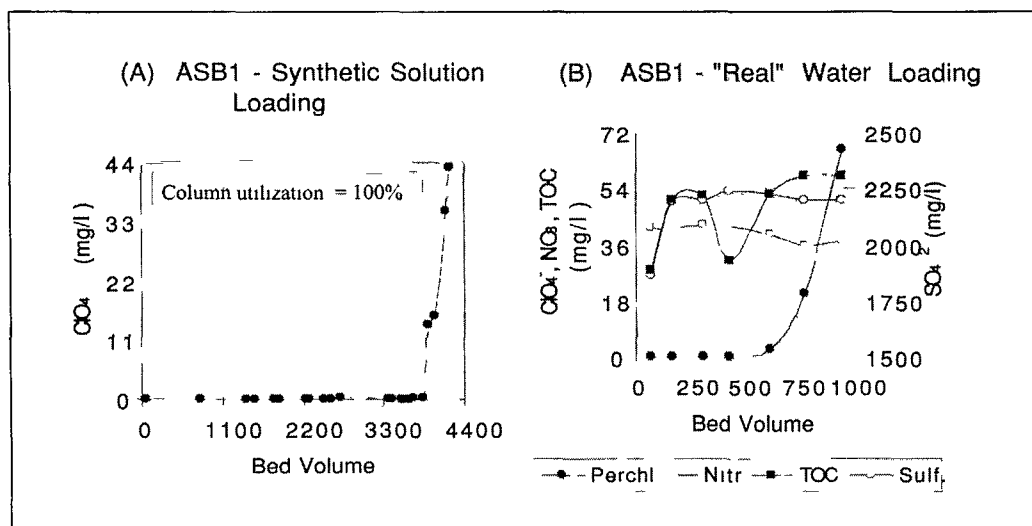


Exhibit 5. Exhaustion of ASB1 resin (styrenic DVB-quaternary amine), (A) fed with 40 mg/l synthetic perchlorate solution, EBCT = 4.9 minutes, BV = 117.84 cm³, total column utilization and column utilization to breakthrough = 100% and (B) fed with the "real" water, EBCT = 4.4 minutes, BV = 114.42 cm³, total column utilization for perchlorate was 48 percent while the column utilization to breakthrough was 22.1 percent

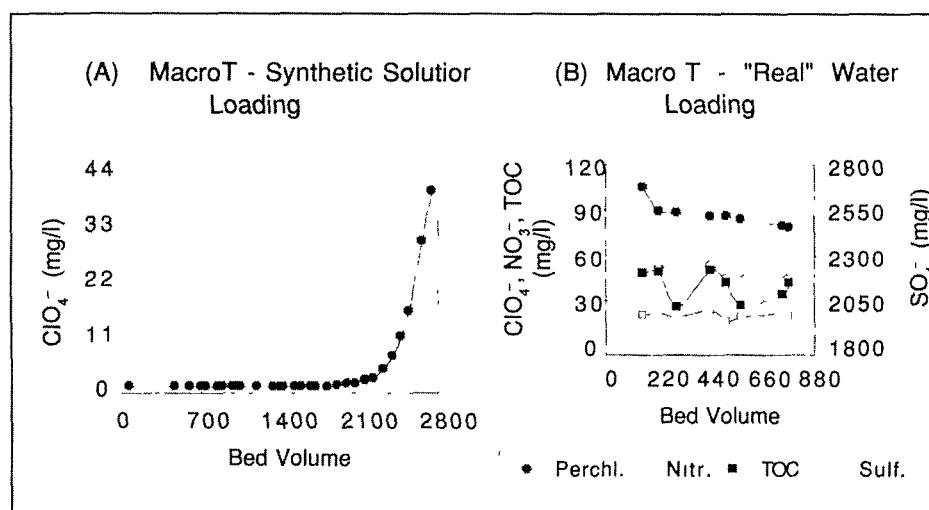


Exhibit 6. Loading of Macro-T resin (polyacrylic-quarternary amine); (A) fed with 40 mg/l synthetic perchlorate solution, EBCT = 4.2 minutes, BV = 54.78 cm³, column utilization to breakthrough = 53.9 percent and total column utilization = 92.7percent; (B) fed with the "real" water, EBCT = 4.5 minutes and BV = 55.49 cm³. The total column utilization for perchlorate approached 0 percent, therefore the column utilization to breakthrough was 0 percent.

on whether the resin is strongly or weakly basic. Strong-base resins are regenerated with salt brines, usually sodium or potassium chloride, 6 to 12 percent in concentration. Weak-base resins can be regenerated with either salt brines or caustic solutions (e.g., 1 percent sodium or ammonium hydroxide). In the case of the selective bifunctional resin cited above, the regenerant is tetrachloroferrate. The waste regenerant solutions resulting from these processes must be treated prior to their disposal in the environment. They contain high concentrations of perchlorate, other anions, and the components of the regenerant solutions. Unfortunately, not much attention has been paid to the development of technologies to treat perchlorate-containing waste solutions from ion-exchange systems. The proprietary PNDM catalytic reduction process developed by Calgon Corporation is the only reported technology that can destroy perchlorate and nitrate in ion-exchange brines. However, because of its proprietary nature, data on the performance, limitation, and costs of this technology have not been reported in open literature.

Biological reduction of perchlorate to innocuous chloride, using several types of reactors, has been demonstrated (Wallace et al., 1998; Attaway & Smith, 1993; Herman & Frankenberger, 1999; Giblin et al., 1999; Hatzinger et al., 2000; Miller & Logan, 2000; Kim & Logan, 2000; Liu & Batista, 2000; Rittmann & Nerenberg, 2000). The process involves the use of perchlorate as an electron acceptor by bacteria in the presence of an electron donor (e.g., carbon source or hydrogen) under anaerobic conditions. Bacteria capable of perchlorate biodegradation are ubiquitous in the natural environment and have been isolated and sequenced from a variety of environments (Coates et al., 1999; Wu et al., 2001). Despite the ubiquity of perchlorate-reducing microorganisms in the natural environment, perchlorate has persisted in groundwaters for as long as 60 years (Boralessa, 2001). Natural perchlorate biodegradation in the environment is limited by lack of electron donor, and high nitrate and salinity levels

(Zhong et al., 2001). However, when the appropriate conditions are present the rate of perchlorate biodegradation is fast. Therefore, biological reduction of perchlorate could possibly be used to treat waste regenerant solutions from ion-exchange systems.

Challenges to Perchlorate Biodegradation in IX Resins Waste Regenerant Solutions

The challenges in using biodegradation to reduce perchlorate in ion-exchange waste solutions reside in the nature of the regenerant and the concentrations of co-anions present.

Nature of Regenerant Solutions

With caustic solutions as the regenerant, there are two issues: (a) high pH (> 11) and (b) high ammonium concentration. Most natural environments have pH values between 5 and 9 and most species have an optimum growth within this range. Very few organisms can grow at extreme pH values. Since perchlorate-reducing bacteria have been isolated from the natural environment within the normal pH range, they are unlikely to grow well at extreme pH values. Thus the pH of caustic IX waste solutions would have to be neutralized with acid to optimize microbial growth. In addition, ionized ammonium ion concentrations greater than 3,000 mg/l (0.3 percent) have been found toxic to microorganisms (Rittmann & McCarty, 2001) and these concentrations should be avoided, if the regenerant brines are to be treated biologically.

Thus the pH of caustic IX waste solutions would have to be neutralized with acid to optimize microbial growth.

When salt brines are used as the regenerant instead of caustic solutions, the concern is the toxicity of salinity to microorganisms. When high salinity is present outside the microbial cell, the osmotic pressure will cause the water contained within the cytoplasm to migrate to the outside of the cell, resulting in cell desiccation and eventual death. There are, however, microbes that can grow at high salinity levels. Microbes that can grow at a salinity of 1M NaCl (5.85 percent) and have no absolute requirement for salt greater than 0.5M NaCl are called halotolerant (Reed, 1986). Bacteria that have a minimum requirement for salt greater than that found in seawater are classified as halophiles. The waste solutions generated from ion-exchange systems typically contain 3–6 percent salts (Gingras & Batista, 2002). The salinity of freshwater is less than 0.05 and that of seawater varies from 3.2 to 3.8 (Reed, 1986). Saturated salt solutions have salinities greater than 30 percent. Microbes living in high-salinity environments have developed the capacity to counter balance the effect of osmotic pressure by accumulating solutes intracellularly, making the salt concentration within the cell greater than in the outside environment. The growth rates of enrichment and pure microbial cultures, known to reduce perchlorate, are shown to severely reduce in the presence of high salinity levels (Gingras & Batista, 2002; Logan et al., 2001).

An evaluation of the composition of the waste solutions obtained when regenerating the selective bifunctional resins with tetrachloroferrate has not been published. Potentially, the waste regenerant solution will have low pH and contain high concentrations of perchlorate, Fe^{+3} , and other anions. If biodegradation of perchlorate and nitrate contained in the waste solution is desired, the pH of the solution has to be increased to around neutral. Potentially, the Fe^{+3} present in the waste solution would be a competing electron acceptor. This is discussed in detail in the following section.

Competition of Other Electron Acceptors

Most perchlorate-reducing microbes are capable of using several other electron acceptors including oxygen, nitrate, and chlorate, but not sulfate (Logan, 2001a). Oxygen and nitrate are used preferentially to perchlorate. An electron donor (e.g., carbon source or hydrogen) has to be provided for the reduction to occur. The added electron donor will be used first to reduce oxygen and nitrate before the perchlorate. Since the waste regenerant solutions from IX systems are likely to contain high concentrations of nitrate, sufficient electron donor has to be provided to sustain nitrate reduction before perchlorate can be reduced. Thus the total cost of providing an electron donor to the process is increased by the presence of nitrate in the brine.

The waste solution from the regeneration of bifunctional resin regeneration with tetrachloferrate is likely to contain high concentrations of Fe^{+3} and low pH. Under anaerobic conditions and in the presence of an electron donor, Fe^{+3} (ferric ion) is biologically reduced to Fe^{+2} (ferrous ion), and preferentially to nitrate. This process is well known and carried out by many organisms that reduce nitrate (Brock & Madigan, 1990). Although studies on the iron-reducing capabilities of perchlorate-reducing bacteria have not been published to date, potentially Fe^{+3} will be reduced preferentially to nitrate and perchlorate.

The pH of the waste solution from this process has to be increased if biodegradation is to take place. However, increasing the pH may promote the formation of iron-containing precipitates that will remove iron from solution and cause operational problems (e.g., scale and clogging). In addition, adjustment of the pH can result in the addition of biologically undesirable ions to the waste. This issue will be discussed in detail later in this article.

Kinetics of Perchlorate Biodegradation

Only a very small number of studies have been published on the kinetics of perchlorate biodegradation (Herman & Frankenberger, 1998; Logan et al., 2001a; Liu, 2000; Gingras & Batista, 2002). However, it is known that perchlorate reduction sustains very high growth rates, similar to those observed when oxygen is used as the electron acceptor. Exhibit 7 shows reported maximum specific growth rates for pure and mixed cultures of perchlorate degrading bacteria. These specific growth rates correspond to doubling times ranging from 3.3 to 69 hours.

The half saturation constant (K_s), the concentration of perchlorate at which the reduction process would proceed half as fast, has been calculated for two perchlorate-reducing isolates as 33 ± 9 and 12 ± 4 mg/l of perchlorate (Logan et al., 2001a). The maximum growth rate (μ_{max}) measured varied from 0.20–0.24 per hour (Logan et al., 2001b). The implication of this finding is that the rate of perchlorate reduction will be slow at low perchlorate concentrations.

The concentration of perchlorate in ion-exchange waste solutions will depend on the composition of the influent water being treated. For waters contaminated with perchlorate on the parts per billion (ppb) range, perchlorate concentration in the waste solutions is expected to be small. For example, the Big Dalton ion-exchange system treating perchlorate concentrations of 18 to 75 ppb produces waste brines with 2–3 mg/l perchlorate (Gingras & Batista, 2002). The same was observed for the pilot ion-exchange plant treating perchlorate-contaminated (50 to 80 ppb) water from Redlands California.

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Culture Type	Electron Donor	Maximum Specific Growth Rates (μ), 1/hr	Reference
Perclace	Acetate	0.07	Herman and Frankenberger, 1998
KJ	Acetate	0.14	Logan et al., 2001
PDX	Acetate	0.21	Logan et al., 2001
Mixed	Lactate	0.010	Gingras & Batista, 2002
Mixed		0.011	Liu, 2000

Exhibit 7. Observed growth rates for mixed and pure cultures of perchlorate reducing microorganisms

That system produces a brine with 3.2 mg/l perchlorate (Gilligly et al., 2002).

For ion-exchange systems treating waters containing perchlorate on the parts per million (ppm) level, the opposite is expected. The brine from ion-exchange columns treating contaminated water with 80 mg/l perchlorate produced brine with 500 mg/l perchlorate (Gingras & Batista, 2002). However, the regenerant solution from a selective bifunctional resin pilot plant is reported to produce a waste solution with 600,000 mg/l perchlorate when treating a water containing 450 μ g/l perchlorate (Gu et al., 2002).

When IX resins are used to treat drinking waters with very low perchlorate concentrations, it is likely that another anion and not perchlorate (e.g., nitrate) will determine the breakthrough point of the resin bed. In this case, the waste solutions would then contain even a smaller concentration of perchlorate than expected. This was observed in the IX pilot plant in Redlands, California, where nitrate controls resin breakthrough (Gilligly et al., 2002). In this case, slow biodegradation kinetics, caused by the small perchlorate concentrations, may be a challenge.

THE PROPOSED TREATMENT SYSTEM

Although perchlorate has been found to occur naturally only in nitrate deposits in Chile (Urbansky et al., 2001), perchlorate-reducing microorganisms have been isolated from a variety of environments (Coates et al., 1999; Wu et al., 2001). Under ordinary environmental conditions, perchlorate reduction proceeds at fast rates. However, under the extreme environmental conditions found in waste solutions from IX regenerant wastes (e.g., high salinity and high ammonium levels), the growth rate of perchlorate-reducing microbes, enriched or isolated under normal environmental conditions, is drastically reduced (Gingras & Batista, 2002). In addition, growth rates of microbial cultures enriched from some saline environments and using perchlorate are shown to be negatively affected at high salinity levels (Logan et al., 2001b).

Given the diversity and abundance of perchlorate-reducing microbes, there may exist microorganisms that are capable of reducing perchlorate under the extreme conditions found in the waste regenerant solutions from IX waste regenerant solutions—and they should be discovered through research.

Biodegradation of Perchlorate at High Salinity and Ammonium Levels

A few studies have been performed to investigate the effects of salinity and high ammonium levels on perchlorate biodegradation. Copolla (1998) observed that a total dissolved solids concentration of 2 to 3 percent hindered perchlorate biodegradation. Gingras and Batista

(2002), using a mixed perchlorate-reducing culture, demonstrated that at salt concentrations as low as 0.5 percent perchlorate biodegradation rate reduced by 30 percent. Perchlorate reduction has been observed in salt concentrations as high as 4.2 percent (Liu, 2000). However, the degradation rates are very slow. (Logan et al. 2001c) demonstrated that three enrichment cultures isolated from seawater, a saline lake water, and biofilm sludge were able to reduce perchlorate at a salinity level of 3 percent with a specific growth rate of 0.057 per day. At a salinity level of 9 percent the growth rate decreased to 0.037 per day. Perchlorate biodegradation in the presence of ammonium has also been investigated. At ammonium concentrations of 0.4 percent and 0.6 percent, perchlorate degradation rate was 90 percent of that when ammonium was not present (Gingras & Batista, 2002). Expected ammonium levels in waste regenerant solutions are below 0.5 percent and further research is needed for ammonium concentrations below 0.5 percent.

To date, what is known about perchlorate biological reduction under extreme conditions is extremely limited. More work is needed to support the development of a technology to biologically treat waste solutions from IX resins. We propose three different system layouts and outline research needs to make the development of this technology possible.

Proposed Waste Regenerant Solution Treatment System for Strong Base IX Resins

Exhibit 8 depicts the proposed system that combines strong base anionic resins for perchlorate removal, and biological reduction for treating the waste brines resulting from resin regeneration. In typical groundwater contaminated with perchlorate, other anions (e.g., SO_4^{2-} , NO_3^- , and HCO_3^-) may also be retained by the resin. If the water to be treated contains a high concentration of sulfate, and/or humic substances, styrenic-type resins are preferred, because they have a lower affinity for sulfate than for perchlorate. On the other hand, acrylic resin should be chosen for waters with low sulfate and low humic acid concentrations, because they regenerate better than styrenic ones.

Strong base resins are generally regenerated with NaCl or KCl and the regenerant waste brines contain 3 to 6 percent salt (Gingras & Batista, 2002). In addition to perchlorate, the brine will contain SO_4^{2-} , NO_3^- , and HCO_3^- , as well as other anions that are also retained by the resins. The ions of the regenerant solution, Cl^- , Na^+ , or K^+ will also be present. Under anoxic conditions and in the presence of an electron donor, both perchlorate (ClO_4^-) and nitrate (NO_3^-) can be reduced biologically to Cl^- and nitrogen gas (N_2), respectively. However, biodegradation of perchlorate, occurring at acceptable rates and at high salinity concentrations has not been demonstrated to date. The proposed system would be feasible if (1) waste brines were diluted to lower salt concentrations (e.g., 2 percent), or (2) halotolerant microbes, capable of perchlorate biodegradation, were isolated.

The research needed to make this system viable include:

1. Search for halotolerant microbes that can utilize perchlorate as an electron acceptor at the desired salinity levels. We believe halotolerant microbes would be more appropriate than halophilic ones because their optimum salinity ranges are generally on a wider range than those of halophilic bacteria. Several halotolerant microorganisms that are capable of nitrate reduction exist. Most perchlorate-reducing microbes can also reduce nitrate; therefore, halotolerant microbes that are capable of perchlorate reduction may exist.

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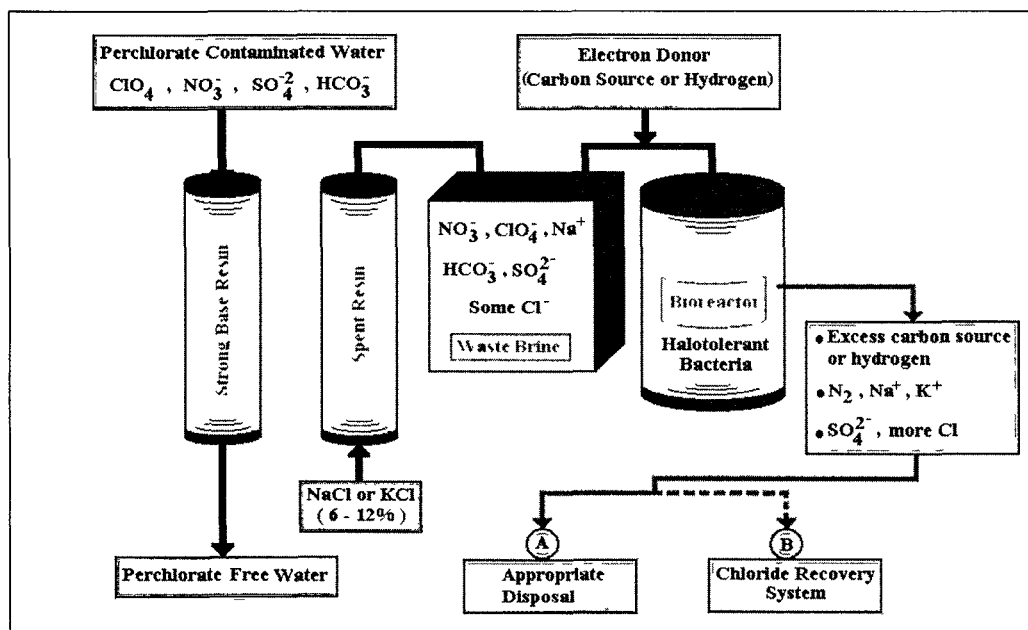


Exhibit 8. Proposed combined system for perchlorate removal using strong-base anionic resins, and biological waste brine reduction of perchlorate and nitrate using halotolerant microorganisms.

2. If halotolerant microbes that can reduce perchlorate are found, determine the biodegradation kinetics of perchlorate using several electron donors. In addition, determine the influence of other electron acceptors, present in the brine, on perchlorate reduction.
3. Investigate the possibility of recycling the chloride resulting from perchlorate biodegradation as a regenerant for spent resins. Assuming halotolerant microorganisms will be isolated that are capable of perchlorate and nitrate reduction, after biodegradation, the waste solution will contain Cl^- ions from two sources; some from the regenerant solution itself (KCl or NaCl) and some resulting from the biodegradation of perchlorate. Assuming a resin with a capacity of 1.0 eq/l, a column utilization of 100 percent and regeneration of the resin with 5 BV of a 12 percent saline solution, the amount of chloride present in the brine after perchlorate biodegradation is estimated to be about 20 percent. Thus a significant amount of chloride can be generated from perchlorate biodegradation. Theoretically, it would be possible to use this chloride as a regenerant, minimizing the cost of regenerant solution. However, there are several issues that have to be considered if such a system is envisioned. One of them is the accumulation of sulfate and sodium ions in the reuse brine. This possibility could be exploited once perchlorate biodegradation on high-salinity brines is proven feasible.

Proposed Waste Regenerant Solution Treatment System for Weak Base IX Resins

Our results demonstrate that acrylic weak-base resins remove perchlorate from waters to very low levels and that they regenerate very well with caustic solutions [$\text{Na}(\text{OH})$ or

$\text{NH}_4(\text{OH})$]. The waste regenerant solutions resulting from this process has high pH that has to be decreased to the neutral range with acid. If sodium hydroxide (NaOH) is used, the brine treatment system would be similar to the one shown in Exhibit 9. The toxicity of salts to perchlorate-reducing microbes relates to the high concentrations of cations (e.g., Na^+ or K^+) and not by the anion chloride. If $\text{NH}_4(\text{OH})$ is used, Na^+ or K^+ will be absent. However, ammonium is toxic to anaerobic systems at concentrations greater than 0.3 percent (3,000 mg/l) (Rittmann & McCarty, 2001). The waste solutions from this system would potentially contain ammonium, perchlorate, nitrate, sulfate, and other anions. There are at least two alternatives to treat the ammonium present in this waste solution: the ammonium could be air stripped or it could be biologically oxidized to nitrate (bioreactor I). Such an approach would increase the concentration of nitrate to be reduced to jointly with perchlorate in the anoxic biological system, bioreactor II. The treated waste solution from this system basically would contain innocuous chloride and nitrogen gas resulting from the biodegradation of perchlorate and nitrate, respectively.

To evaluate the feasibility of this system, the research needs are:

1. Investigation of the best alternative to remove the ammonium from the waste regenerant solution.
2. If ammonia is to remain in the biological system as a source of nitrogen, evaluate the influence of ammonium levels smaller than 3,000 mg/l on the biological reduction rates of perchlorate.
3. Determine the kinetics of perchlorate reduction in the regenerant solution in the presence of several electron donors and acceptors.

Proposed Waste Regenerant Solution Treatment System for

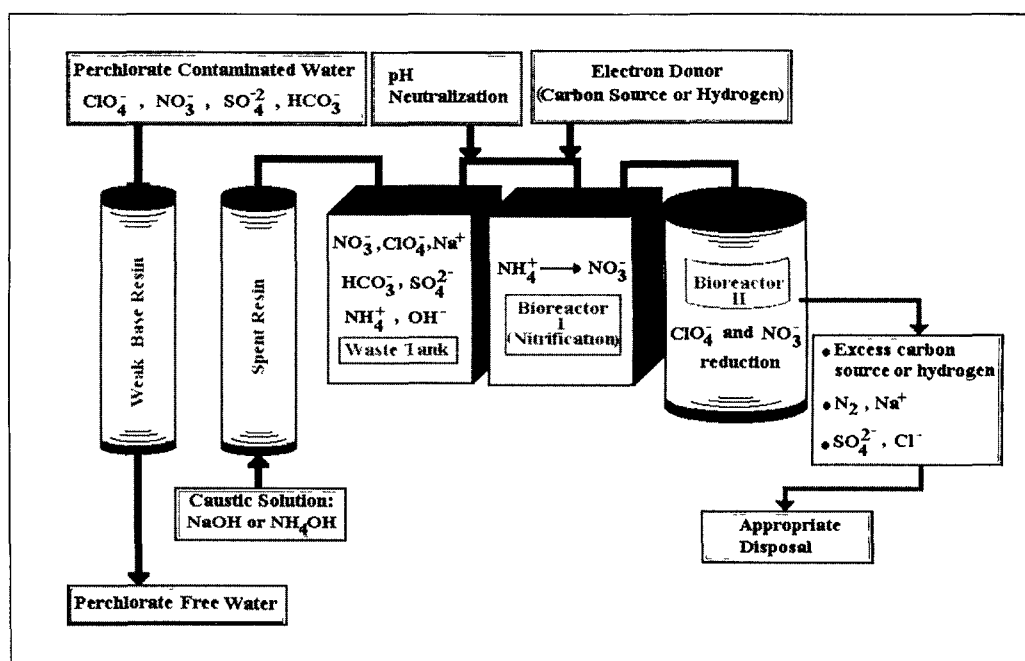


Exhibit 9. Proposed combined perchlorate removal system using weak-base anionic resin and biological reduction of perchlorate and nitrate contained in the waste regenerant solution.

Perchlorate Selective Resins

Tetrachloroferrate (FeCl_4^-) has been shown to successfully regenerate selective bifunctional resins loaded with perchlorate. The waste regenerant solution resulting from the system in which tetrachloroferrate is used will contain high perchlorate concentrations, other anions, low pH, and high concentrations of Fe^{+3} . No preliminary work has been performed to determine the feasibility of perchlorate biodegradation in the waste solution generated in this system. An adjustment to the pH will be needed to increase the pH of the regenerant solution. If NaOH is added, then the Na^+ will be toxic to the microbes, and we have a waste treatment strategy similar to that proposed for spent brines of strong-base resins. If ammonium hydroxide is used, then we will have a situation similar to that proposed for weak-base waste regenerant solutions. However, if the amount of base needed to increase the pH to the desired level is not significantly high to increase the concentrations of Na^+ and NH_4^+ , the treatment system proposed in Exhibit 10 could be used. The system would not require the use of halotolerant microbes and one drawback would be the extra electron donor need to reduce Fe^{+3} to Fe^{+2} . However, there are many unknowns regarding the composition of the tetrachloroferrate water regenerant solution and further discussion would constitute mere speculation. Research needs for this system include:

1. Determination of the potential pH and Fe^{+3} of the spent waste regenerant solution.
2. Evaluation of the most plausible alternative to neutralize the pH of waste solution.
3. Investigation of the influence of Fe^{+3} reduction on perchlorate and nitrate removal by perchlorate-reducing microorganisms.
4. Determination of the impact of Fe^{+2} on the overall disposal of the treated waste solution.

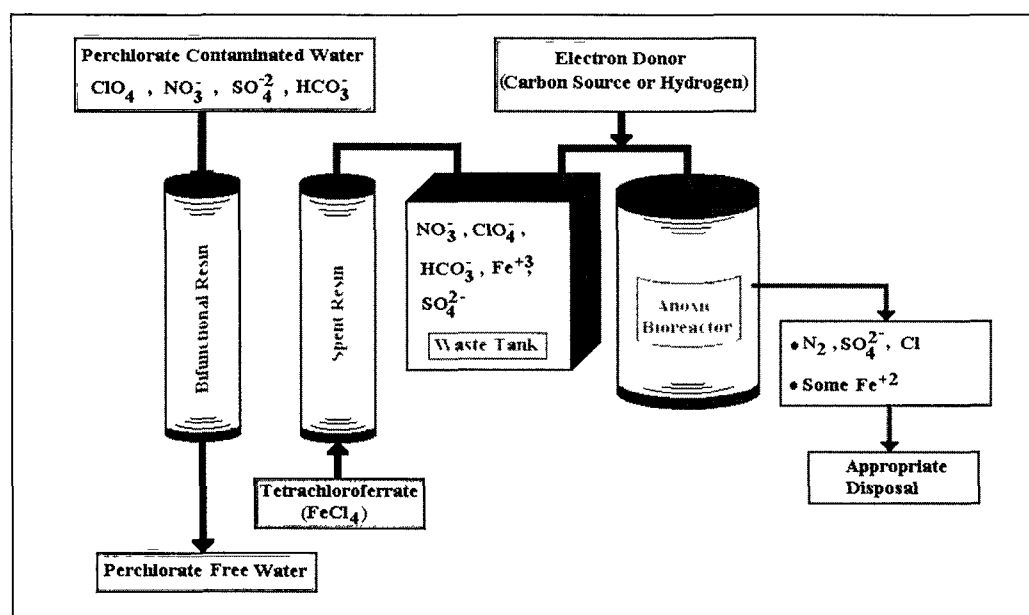


Exhibit 10. Proposed combined perchlorate removal system using perchlorate-selective resins and biological reduction of perchlorate, nitrate, and Fe^{+3} contained in the waste regenerant solution.

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